Variation Principle for Calculation of Many-Particle Effects in Crystals

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Abstract

Variation principle has been developed to calculate many-particle effects in crystals. Within the framework of quasi-particle concept the variation principle has been used to find one-electron states with taking into account of effects due to non-locality of electronic density functional in electromagnetic fields. A secondary quantized density matrix was used to find the Green function of a quasiparticle and changes of its effective mass due to correlated motion of interacting electrons.

1 Introduction

Because of high dimensionality the complexity of many-electron problems all problems of a solid state physics of this type are much higher than of one-electron problem. Results of a solution of the one-electron problem can be utilized in many-electron problems in solid state physics if one supposes that motion of an electron happens in a self-consistent one-particle potential $V(\vec{r})$. The self-consistent potential is yielded by the solution of the Poisson equation, for which the density of one-electron states is a self-consistent solution of the one-particle Hartree - Fock equations [1] - [4]. These equations have been written originally to calculate one-particle states of many-electron atom. Equations of the Hartree - Fock type for band calculations have been proposed by Kohn and Sham [5]. It is practically impossible to look for their solution without additional assumptions if many-particle effects are circumscribed by distributed in space electron density functional. One of them is that one-particle solutions describe a crystal as a set of interacting quasiparticle excitations [6]. In a given paper we offer an approach which allows to determine one-electron states with taking into account of the effects owing to a non-locality of electron density functional in electromagnetic fields and which is based on usage of the variation principle.

2 A variational principle for band calculations

Let us write a one-electron Hartree - Fock Hamiltonian for a system of N electrons, $N \to \infty$, moving in a field originated by atoms nucleus' of a crystal

$$\left[\frac{1}{2}\hat{p}_i^2 + U(r_i) + \hat{V}^{sc}(\vec{r}_i, \sigma_i) - \hat{\Sigma}^x(\vec{r}_i, \sigma_i)\right] \psi_n(k_i r_i) =$$
$$= (\epsilon_n(0) + \epsilon_n(k_i))\psi_n(k_i r_i) \tag{1}$$

with a unit choice $\hbar = 1$, $m = 1$, where $\hat{p}_i^2/2 = -\frac{1}{2}\triangle(\vec{r}_i)$ is a kinetic energy in system of atomic units, $\triangle(\vec{r}_i)$ is the Laplacian operator written in a given point with a radius-vector $\vec{r}_i$ in which i-th electron having a spin σ_i is situated; $U(r_i)$ is potential energy of i-th electron in nucleus field of the crystal, $\hat{V}^{sc}$ and $\hat{\Sigma}^x$ are operators of Coulomb and exchange interactions, respectively [7]:

$$\hat{V}^{sc}(\vec{r}_i, \sigma_i)\psi_n(k_i r_i) = \sum_{m=1}^{N} \int \psi_m^*(k_i r_i')v(|\vec{r}_i - \vec{r}_i'|)\psi_m(k_i r_i') \; dr_i'\psi_n(k_i r_i),$$

(2)

$$\hat{\Sigma}^x(\vec{r}_i, \sigma_i)\psi_n(k_i r_i) = \sum_{m=1}^{N} \int \psi_m^*(k_i r_i')v(|\vec{r}_i - \vec{r}_i'|)\psi_n(k_i r_i') \; dr_i'\psi_m(k_i r_i);$$

(3)

$r_i \equiv \{\vec{r}_i, \sigma_i\}$, $\psi_n(k_i r_i)$ is a wave function including spin and coordinate parts, $v(|\vec{r}_i - \vec{r}_i'|)$ is potential energy of electron interaction. The physical sense of the operators (2, 3) becomes obvious if one rewrites them in terms of spin-zero electronic density $\rho(\vec{r}, \vec{r}')$ and assumes that the interaction v is the Coulomb one:

$$\rho(\vec{r}, \vec{r}') = \frac{1}{2}\sum_{m=1}^{N-1} \left(\psi_m^*(\vec{k} \cdot \vec{r}, \sigma)\psi_m(\vec{k} \cdot \vec{r}', -\sigma) + \psi_m^*(\vec{k} \cdot \vec{r}, -\sigma)\psi_m(\vec{k} \cdot \vec{r}', \sigma) \right)$$

$$= \sum_{m=1}^{(N-1)/2} \psi_m^*(\vec{k} \cdot \vec{r})\psi_m(\vec{k} \cdot \vec{r}'), \quad v = e^2/|\vec{r} - \vec{r}'|.$$

(4)

It follows from here that the operator $\hat{V}^{sc}$ gives electrostatic interaction of one electron with an electron density created by residual $N-1$ electrons, with an electrostatic self-action (s.a.):

$$\hat{V}^{sc}(\vec{r}_i, \sigma_i)\psi_n(k_i r_i) = \sum_{\sigma}\sum_{m=1}^{(N-1)/2} \int \psi_m^*(\vec{k}_i \cdot \vec{r}_i')v(|\vec{r}_i - \vec{r}_i'|)\psi_m(\vec{k}_i \cdot \vec{r}_i') \; d\vec{r}_i'\psi_n(\vec{k}_i \cdot \vec{r}_i) + \text{s.a.}$$

$$= 2\int d\vec{r}_i'\frac{e^2\rho(\vec{r}_i', \vec{r}_i')}{|\vec{r}_i - \vec{r}_i'|}\psi_n(k_i r_i) + \text{s.a.} \quad (5)$$

Analogously we get that the operator $\hat{\Sigma}^x$ gives a quantum exchange with an exchange self-action (s.a.):

$$\hat{\Sigma}^x(\vec{r}_i, \sigma_i)\psi_n(k_i r_i) = \sum_{m=1}^{N-1} \int\int dr_j d\sigma_j \psi_m^*(\vec{k}_i \cdot \vec{r}_j, \sigma_j)v(|\vec{r}_i - \vec{r}_j|)\psi_n(k_i \cdot \vec{r}_j, \sigma_j)\psi_m(\vec{k}_i \cdot \vec{r}_i, \sigma_i)$$

$$= \frac{1}{2}\sum_{m=1}^{N-1} \int\int dr_j d\sigma_j \left(\psi_m^*(\vec{k} \cdot \vec{r}_j, \sigma_j)\psi_m(\vec{k} \cdot \vec{r}_i, -\sigma_j)\delta(\sigma_j - \sigma_i) \right.$$

$$\left. + \psi_m^*(\vec{k} \cdot \vec{r}_i, -\sigma_j)\psi_m(\vec{k} \cdot \vec{r}_j, \sigma_j)\delta(\sigma_j - \sigma_i) \right) v(|\vec{r}_i - \vec{r}_j|)\psi_n(k_i \cdot \vec{r}_j, \sigma_j) + \text{s.a.}$$

$$= \int d\vec{r}_j\frac{e^2\rho(\vec{r}_j, \vec{r}_i)}{|\vec{r}_i - \vec{r}_j|}\psi_n(k_i r_j) + \text{s.a.} \quad (6)$$

Since operators $\hat{V}^{sc}$ and $\hat{\Sigma}^x$ in expression (1) are subtracted one from another the self-acting terms vanish.

A quantity $\epsilon_n(k_i)$ entering in expansion $E_n(k_i) = f(\epsilon_n(0)) + \epsilon_n(k_i)$ being n-th eigenvalue $E_n(k_i)$ of the Hamiltonian for N particles system in Hartree -Fock approximation is the energy of n-th band. A quantity $\epsilon_n(0)$ determines a reference point $\mathrm{Extr} E_n(k_i) = f(\epsilon_n(0))$ of n-th bands, where f is an unknown function. Within the framework of quasiparticle concept the physical sense of $\epsilon_n(k_i)$ is the energy of quasiparticle excitation.

Let us take a solution of one-electron problem for an atomic area in a cell potentials approximation as $\epsilon_n(0)$ and a basic set on which one constructs an expansion of a trial function $\widetilde{\psi}_n(k_i r_i)$ of n-th band. Then one can realize a variational principle as the following expression:

$$\delta \epsilon_n[\widetilde{\psi}_n] = 0, \tag{7}$$

which is determined not strictly as it is used to find excited states for which, as a rule, the basic set of functions is unknown [7].

Let us show, that the variational principle for excited states in the form (7) can be made strictly determined one. Since, by definition, the energy of a nonexcited state coincides with an extremum of a functional $E_n[\widetilde{\psi}_n]$ we have the following equality of variations:

$$\delta \epsilon_n[\widetilde{\psi}_n] = \delta E_n[\widetilde{\psi}_n] = 0. \tag{8}$$

The ambiguity of a variation (8) consists only in an arbitrariness of a position of a reference point for an energy band as the variation procedure for an one-electron problem is strictly determined. If a symmetry of atomic areas is definite and a cell partition of the crystalline space is unambiguous then, in principle, this arbitrariness is removed easy by utilizing the quasi-particles concept, according to which

$$\epsilon_n(k_i) = \epsilon_n(-k_i). \tag{9}$$

It follows from the expressions (8) and (9), that the additional variation of a reference point of a band gives a coincidence of this point with a centre of the energy band for a crystal and allows to transform the variational principle (8) finding noninteracting quasiparticles states to strictly determined expression

$$\delta E_n[\widetilde{\psi}_n] = 0, \quad \delta f[\widetilde{\psi}_n] = 0. \tag{10}$$

Let us find the reference point $\mathrm{Extr} E_n(k_i)$ of energy band using a method of density matrix functional.

3 Secondary quantized reduced density matrix

As is known [8], equations in quantum mechanics can be written not for a wave function, but for a density matrix ρ. The operator ρ is a projective operator for pure states and can be presented in terms of Dirac ket(bra)-vectors as $\rho = |\psi\rangle\langle\psi|$. If the operator ρ is known then we can find, by definition, energy E of system of N particles, described by a Hamiltonian $\hat{H}(\vec{r}_1, \dots, \vec{r}_N)$ and a wave function $|\psi\rangle$ as

$$E = \mathrm{Sp}\, \rho \hat{H}. \tag{11}$$

Let us introduce n-dimensional density matrix ρ_n by

$$\rho_n(\vec{r}_1', \ldots, \vec{r}_n'; \vec{r}_1, \ldots, \vec{r}_n) = \frac{N!}{(N-n)!} \int d\vec{r}_{n+1} \ldots d\vec{r}_N$$
$$\times \langle \vec{r}_1', \ldots, \vec{r}_n', \vec{r}_{n+1}, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_n, \vec{r}_{n+1}, \ldots, \vec{r}_N \rangle, \tag{12}$$

which, by implication, is a reduced coordinate distribution n-particle function [9]. By definition, it has a normalization

$$\mathrm{Sp}\rho_n = \frac{N!}{(N-n)!} \quad n = 1, \ldots, N. \tag{13}$$

Let us examine the system consisted of N with a pairwise interaction

$$\sum_{i>j=1}^{N} v(|\vec{r}_i - \vec{r}_i'|).$$

Then, since projective operators possess the following properties: $\rho^2 = \rho$ and $\rho^* = \rho$ the expression (11) is transformed to the form:

$$E = \mathrm{Sp}\, \rho \left(\hat{H}_0 + \sum_{i>j=1}^{N} v(|\vec{r}_i - \vec{r}_j|) \right) = \mathrm{Sp}\, \rho \sum_{i=1}^{N} \hat{h}(\vec{r}_i) + \mathrm{Sp}\, \rho^2 \sum_{i>j=1}^{N} v(\vec{r}_i, \vec{r}_j) =$$
$$= \mathrm{Sp}\, \rho \sum_{i=1}^{N} \hat{h}(\vec{r}_i) + \mathrm{Sp}\, |\rho|^2 \sum_{i>j=1}^{N} v(\vec{r}_i, \vec{r}_j), \tag{14}$$

where $\hat{h}(\vec{r}_i) = \frac{1}{2}\hat{p}_i^2 + U(r_i)$. Since the non-perturbed hamiltonian $\hat{H}_0$ in Eq. (14) consists of independent one-particle summands and interaction of particles occurs pairwise, the operator of trace appears in Eq. (14) over one variable r_1 and two variables r_1, r_2:

$$E = \mathrm{Sp}\, \sum_{i=1}^{N} \hat{h}(\vec{r}_1) \int d\vec{r}_2 \ldots d\vec{r}_N$$
$$\times \langle \vec{r}_1', \vec{r}_2, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_N \rangle + \mathrm{Sp}\, \sum_{i>j=1}^{N} v(|\vec{r}_1 - \vec{r}_2|)$$
$$\times \frac{1}{2} \left[\int d\vec{r}_1 d\vec{r}_3 \ldots d\vec{r}_N \left| \langle \vec{r}_1, \vec{r}_2', \vec{r}_3, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_N \rangle \right|^2 \right.$$
$$\left. + \int d\vec{r}_2 \ldots d\vec{r}_N \left| \langle \vec{r}_1', \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_N \rangle \right|^2 \right], \tag{15}$$

Using the equality: $\int \vec{k} \cdot \vec{k} d\theta = 2|k|^2$ one can transform Eq. (15) and obtain:

$$E = \text{Sp } \hat{h}(\vec{r}_1)N \int d\vec{r}_2 \ldots d\vec{r}_N$$

$$\times \langle \vec{r}_1', \vec{r}_2, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_N \rangle + \frac{1}{4} \text{ Sp } v(|\vec{r}_1 - \vec{r}_2|)N(N-1)$$

$$\times \left[\int d\vec{r}_1 d\vec{r}_3 \ldots d\vec{r}_N \langle \vec{r}_1, \vec{r}_2', \vec{r}_3, \ldots, \vec{r}_N | \psi \rangle \times \right.$$

$$\times \int d\vec{r}_2 \ldots d\vec{r}_N \langle \psi | \vec{r}_1', \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N \rangle \langle \vec{r}_1, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_N \rangle$$

$$+ \int d\vec{r}_2 \ldots d\vec{r}_N \langle \vec{r}_1', \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N | \psi \rangle \times$$

$$\left. \times \int d\vec{r}_1 d\vec{r}_3 \ldots d\vec{r}_N \langle \psi | \vec{r}_1, \vec{r}_2', \vec{r}_3, \ldots, \vec{r}_N \rangle \langle \vec{r}_1, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_N \rangle \right].$$

$$(16)$$

It is easy to see, that the first summand from the right-hand side of Eq. (16) contains the reduced one-particle density matrix ρ_1 as a multiplier. Therefore after some obvious transformations Eq. (16) can be rewritten as:

$$E = \text{Sp } \hat{h}(\vec{r}_1)\rho_1(\vec{r}_1', \vec{r}_1) + \frac{1}{2}\text{Sp } v(|\vec{r}_1 - \vec{r}_2|)N(N-1)$$

$$\times \int d\vec{r}_3 \ldots d\vec{r}_N \langle \vec{r}_1', \vec{r}_2', \vec{r}_3, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N \rangle \times$$

$$\times \int d\vec{r}_1 d\vec{r}_2 \ldots d\vec{r}_N \langle \vec{r}_1, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \ldots, \vec{r}_N \rangle$$

$$= \text{Sp } \hat{h}(\vec{r}_1)\rho_1(\vec{r}_1', \vec{r}_1) + \frac{1}{2}\text{Sp } v(|\vec{r}_1 - \vec{r}_2|)N(N-1)$$

$$\times \int d\vec{r}_3 \ldots d\vec{r}_N \langle \vec{r}_1', \vec{r}_2', \vec{r}_3, \ldots, \vec{r}_N | \psi \rangle \langle \psi | \vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N \rangle.$$

$$(17)$$

Here one takes into account the normalization of wave function $|\psi\rangle$: $\int \langle \psi | \psi \rangle \, d\vec{r}_1 d\vec{r}_2 \ldots d\vec{r}_N = 1$.

If we observe that in the right side of the equation (17) the second summand contains the reduced two-particle density matrix ρ_2 as a multiplier then it is possible to transform this equation to the expression which has the reduced density matrixes ρ_1 and ρ_2:

$$E = \text{Sp } \hat{h}(\vec{r}_1)\rho_1(\vec{r}_1', \vec{r}_1) + \frac{1}{2}\text{Sp } v(|\vec{r}_1 - \vec{r}_2|)\rho_2(\vec{r}_1', \vec{r}_2'; \vec{r}_1, \vec{r}_2) =$$

$$= \epsilon^{(0)}N + \frac{1}{2}\text{Sp } v(|\vec{r}_1 - \vec{r}_2|)\rho_2(\vec{r}_1', \vec{r}_2'; \vec{r}_1, \vec{r}_2), \qquad (18)$$

where $\epsilon^{(0)}$ is the one-electron state, the summand $E^{HF} = \frac{1}{2}\text{Sp } v(|\vec{r}_1 - \vec{r}_2|) \, \rho_2(\vec{r}_1', \vec{r}_2'; \vec{r}_1, \vec{r}_2)$ is excitation energy of the system under the interaction. Since in the Hartree - Fock approximation the reduced density matrix ρ_2 is factorized, at first, the energy $\epsilon^{(0)}N$ equal to energy of N one-electron states, including kinetic energy of an electron, energy of an electron in a self-consistent scalar potential, and exchange energy, and, secondly, energy E^{HF} of the

excitation yield, as it follows from the equations (1) and (18), a contribution to the electronic energy E of a crystal. Further we shall show, that the Hartree - Fock approximation is an one-particle approximation in the sense that in this approximation the excitation energy E^{HF} is represented as the energy of quasiparticle states.

Now, we rewrite Eq. (1) in the representation of Dirac ket(bra)- vectors:

$$\hat{h}(k)|n;k\rangle + \sum_{m=1,m\neq n}^{N} \int \delta(k-k')\ dk'(|n;k\rangle\langle m;k'|v(kk')|m;k'\rangle +$$

$$+(|n;k'\rangle\delta_{nm})\langle m;k'|v(kk')(|m;k\rangle\delta_{mn}))$$

$$-\sum_{m=1}^{N}\int|m;k\rangle\langle m;k'|v(kk')|n;k'\rangle\delta(k-k')\ dk' =$$

$$= |n;k\rangle(\epsilon_n(0) + \epsilon_n(k)) \tag{19}$$

where $k_i \equiv \{\vec{k}_i, \sigma_i\}$, $\hat{h}(k)$ is a momentum representation of the non-perturbed hamiltonian, $v(kk') = \int d\vec{r}d\vec{r'}|\vec{r}\rangle\langle\vec{k}\cdot\vec{r}|v(|\vec{r}-\vec{r'}|)|\vec{k'}\cdot\vec{r'}\rangle\langle\vec{r'}|$ is a momentum representation of the Coulomb interaction operator, $\delta(k-k')$ is the Dirac δ-function manifesting the presence of the law of conservation of momentum.

Let us introduce projective operators $\hat{\rho}_{kk'}^{mn}$

$$\hat{\rho}_{kk'}^{mn} \equiv |m;k'\rangle\langle n;k| \tag{20}$$

and express Eq. (19) via these operators $\hat{\rho}_{kk'}^{mn}$. For this purpose, Eq. (19) is multiplied on the right by bra-vector $\langle n;k|$. Then, additional summating over n and integrating over dk one get the equation:

$$\sum_{n=1}^{N}\int dk\ \hat{h}(k)|n;k\rangle\langle n;k| + \sum_{n=1}^{N}\int\int\delta(k-k')\ dk\ dk' \times$$

$$\times|n;k\rangle\sum_{m=1}^{N}\langle m;k'|v(k,k')|m;k'\rangle\langle n;k| + \int\int\delta(k-k')\ dk\ dk' \times$$

$$\times\left(\sum_{m=1}^{N}|n;k'\rangle\delta_{nm}\langle m;k'|\right)v(kk')\left(\sum_{n=1}^{N}|m;k\rangle\delta_{mn}\langle n;k|\right) -$$

$$-\int\int\sum_{m=1}^{N}|m;k\rangle\langle m;k'|v(kk')\sum_{n=1}^{N}|n;k'\rangle\langle n;k|\delta(k'-k)d(-k)d(-k')$$

$$= \int dk\sum_{n=1}^{N}\langle n;k|n;k\rangle(\epsilon_n(0) + \epsilon_n(k)). \tag{21}$$

We see that the first and second terms on the left of the equation (21) are traces of a matrix representation of operators $\hat{\rho}\hat{h}$ and $\hat{\rho}^*\hat{\rho}v$, and the third and fourth terms on the left of equation (21) are mutually cancelled. Hence, it means that using normability of function $|n;k\rangle$: $\int dk\langle n;k|n;k\rangle = 1$, we obtain the following equation:

$$\mathrm{Sp}\hat{\rho}\hat{h} + \mathrm{Sp}\hat{\rho}^*\hat{\rho}v = \epsilon_n(0)N + \int dk\sum_{n=1}^{N}\langle n;k|n;k\rangle\epsilon_n(k). \tag{22}$$

Using properties of the projective operators $\hat{\rho}_{kk'}^{mn}$: $(\hat{\rho}_{kk'}^{mn})^* = \hat{\rho}_{kk'}^{mn}$ and $(\hat{\rho}_{kk'}^{mn})^2 = \hat{\rho}_{kk'}^{mn}$ one can transform Eq. (22) to the form:

$$\mathrm{Sp}\hat{\rho}(\hat{h} + v) = \epsilon_n(0)N + \int dk \sum_{n=1}^{N} \langle n; k|n; k\rangle \epsilon_n(k) = \epsilon_n(0)N + \epsilon. \tag{23}$$

Let us elucidate a physical sense of introduced projective operators $\hat{\rho}_{kk'}^{mn}$. It follows from comparison (18) and (23) that the energy of a quasi-particle ϵ is on the right of Eq. (23) accurate to the constant $\epsilon_n(0)N$. It follows from here that the operator $\hat{\rho}_{kk'}^{mn}$ allows to calculate energy ϵ of quasiparticle excitations. It means that the expression (23) is nothing else but a procedure of average on density matrix. Since the averaging with the help of the operator $\hat{\rho}_{kk'}^{mn}$ yields energy ϵ of quasi-particle this operator is a secondary quantized density matrix.

It follows from the comparison of right sides of the equations (1), (18), and (23) that the reference point $\mathrm{Extr}E_n(k_i)$ of energy band determines the solution $\epsilon_n(0)$ of the one-electron problem

$$\epsilon_n(0) = \mathrm{Extr}\ E_n(k_i)/N. \tag{24}$$

Thus, one has proved that the equation (1) can be considered as an equation describing a state of quasi-particle and determining its energy accurate to the constant $\epsilon_n(0)N$.

4 Green function for one-particle state

It follows from Eq. (23) also that the quantity $\epsilon_n(k_i)$ can be interpreted as an eigenvalue of the Hamiltonian for the quasi-particle excitation without taking into account interaction of quasi-particles. Therefore, the equation (23), written in the formalism of density matrix $\hat{\rho}_{nn';kk'}^{(0)} \equiv \hat{\rho}_{kk'}^{mn}$ can be rewritten in the formalism of wave functions in coordinate representation and in a limit of large N, $N \to \infty$ in the following way:

$$\left(\imath\frac{\partial}{\partial t} - (\hat{h} + \Sigma^x + V^{sc})\right) \sum_n \hat{\rho}_{nn';rr'}^{(0)} = \lim_{N\to\infty} (-\epsilon_n(0))N\delta_{rr'}, \tag{25}$$

where property $\int dk\langle n; kr|n; kr'\rangle = \delta_{rr'}$ has been used; $\delta_{rr'}$ is a delta symbol. Since the energy $\epsilon_n(0)$ of the bound one-electron state is negative: $\epsilon_n(0) < 0$, the right side of Eq. (25) represents itself a Dirac δ-function $\delta(r - r')$. It allows to write Eq. (25) as:

$$\left(\imath\frac{\partial}{\partial t} - \hat{h}^{HF}\right) \sum_n \hat{\rho}_{nn';r,r'}^{(0)} = \delta(r - r'), \tag{26}$$

where $\hat{h}^{HF} = (\hat{h} + \overline{\Sigma}^x + V^{sc})$, $\overline{\Sigma}^x = -\Sigma^x$. Eq. (26) is the equation for the Green function. It means that in the secondary quantized representation an operator

$$\hat{G}_1^{(0)}(n'; r, r') = \sum_n \hat{\rho}_{nn';r,r'}^{(0)} \tag{27}$$

possesses properties of non-perturbed Green function.

So, the quasi-particle excitation determined by the Hamiltonian $\hat{h}^{HF}$ can be considered as a free particle whose equation of motion is the equation (26).

In the many-body problem, in particular, in calculations of an energy-band crystal structure a contribution given by interaction of electromagnetic field with matter is played the essential role. To take into account many-particle effects due to a correlated motion of electron we should describe the system by self-consistent solutions of the non-stationary equation

$$\imath \frac{\partial \Psi(t)}{\partial t} = \hat{H}\Psi(t) \tag{28}$$

where $\hat{H}$ is a Schrödinger hamiltonian in a non-relativistic case or a Dirac hamiltonian in a relativistic case. It turns the variational principle (10) into a variational principle for the excited states, not being strictly definite one. Further, we shall show that within the framework of the concept of quasiparticle excitations this ambiguity can be removed by means of the account of interaction as, at first, a change of a quasi-particle mass and, second, as a changing of the location of reference point of energy band.

We have proved that for the secondary quantized representation the operator ρ looks as $\hat{\rho} = |\hat{\psi}\rangle\langle\hat{\psi}|$ and possesses properties of the Green function G_1. Therefore the sum $\hat{G}_1$ over n from elements of the matrix $\hat{\rho}_{kk'}^{nn'}$ for the secondary quantized density matrix $\hat{\rho}$ describing an interacting particle satisfies a Dyson equation in a nonrelativistic case or to a Schwinger - Dyson equation in a relativistic case:

$$G_1(1;2) = G_1^{(0)}(1;2) + \int d3 \, d4 \, G_1^{(0)}(1;3)\hat{\Sigma}(3,4)G_1(4;2) \tag{29}$$

$G_1^{(0)}(1;2)$ is a free Green function, $\hat{\Sigma}(3,4)$ is a self-energy operator: $\hat{\Sigma} = \overline{\Sigma}^x + \hat{\Sigma}^c$, $\hat{\Sigma}^c$ is a correlation interactions, representing itself a part of the self-energy which describes the many-particle effects. Here numerical labels for the arguments are used: $\{r_1, t_1\} = x_1 \equiv 1$, etc. Acting on Eq. (29) by the operator $\imath\frac{\partial}{\partial t} - \hat{h}^{HF}$ and using the equation of motion for the free particle (26) we get the equation for the perturbed Green function as

$$\left[\imath\frac{\partial}{\partial t} - \hat{h}^{HF}(r_1)\right] G_1(n';1,2) - \int d3\hat{\Sigma}^c(n';1,3)G_1(n';3,2) =$$
$$= (-\epsilon_n(0))N\delta_{r_1 r_2}. \tag{30}$$

Rewriting Eq. (30) in the formalism of wave functions one gets

$$\left[\imath\frac{\partial}{\partial t} - \hat{h}^{HF}(r_1)\right] \psi_n(k_1 r_1) - \int d\vec{r}_2\hat{\Sigma}^c(n;1,2)\psi_n(k_1 r_2) =$$
$$(-\epsilon_n(0))\psi_n(k_1 r_1). \tag{31}$$

Since the expression: $\imath\frac{\partial\psi_n}{\partial t} = \epsilon_n(k_1)$ takes place, then Eq. (31) yields the Hartree - Fock taking into account of interacting quasi-particles

$$\hat{h}^{HF}(r_1)\psi_n(k_1 r_1) + \int d\vec{r}_2\hat{\Sigma}^c(n;1,2)\psi_n(k_1 r_2) =$$
$$= (\epsilon_n(0) + \epsilon_n(k_1))\psi_n(k_1 r_1). \tag{32}$$

Let us define a mass operator $\widehat{\Delta M}$ as:

$$\widehat{\Delta M}\psi_n(k_1 r_1) = \int d\vec{r}_2 \hat{\Sigma}^c(n; 1, 2)\psi_n(k_1 r_2). \tag{33}$$

Within the framework of the concept quasiparticle excitations it is possible to represent the operator $\widehat{\Delta M}$ in the diagonal form:

$$\widehat{\Delta M}\psi_n(k_i r_i) = (\Delta M_n(0) + \Delta M_n(k_i))\psi_n(k_i r_i). \tag{34}$$

It is known that the eigenvalue of mass operator possesses the property: $\Delta M_n(k_i) = \Delta M_n(-k_i)$. Here $\Delta M_n(0)$ is an eigenvalue of mass operator $\widehat{\Delta M}$ in the limit $\vec{k} \to 0$.

It follows from here the physical sense of $\widehat{\Delta M}$. It determines an effective mass of the quasi-particle and an efficient reference point of the energy band:

$$\hat{h}^{HF}(r_1)\psi_n(k_1 r_1) = (\tilde{\epsilon}_n(0) + \tilde{\epsilon}_n(k_1))\psi_n(k_1 r_1) \equiv$$
$$\equiv [(\epsilon_n(0) + \Delta M_n(0)) + (\epsilon_n(k_1) + \Delta M_n(k_1))] \psi_n(k_1 r_1). \tag{35}$$

Since the change of the mass of quasi-particle determined by the operator $\widehat{\Delta M}$ maintains the condition (9) then if to take into account the change of the reference point of band at interaction, the variational principle for the interacting system becomes a strictly definite one and takes the form:

$$\delta E_n[\widetilde{\psi}_n] = 0, \quad \epsilon_n(0) = \frac{1}{N}\text{Extr}E_n(k_i) - \Delta M_n(0). \tag{36}$$

Equation of motion for one-particle state and basis set of wave functions for exited atom

Let us consider a Green function normalized per unit volume $V = 1$ so that an average energy in V is equal to the energy of the one-particle state and $N = 1$. If $-\epsilon_n(0) \to \infty$ then Eq. (30) describes a propagation of one particle and should be rewritten as

$$\left[i\frac{\partial}{\partial t} - \hat{h}^{HF}(r_1)\right] G_1(n'; 1, 2) - \int d3\hat{\Sigma}^c(n'; 1, 3)G_1(n'; 3, 2) =$$
$$= (-\epsilon_n(0))\delta_{r_1 r_2}. \tag{37}$$

It follows from here that according to the definition of Green functions we have the following expression for the energy $\epsilon_n(0)$:

$$-\epsilon_n(0) = C - a_n, \quad C \to \infty; \tag{38}$$

where a_n is a finite quantity. Hence, since the energy is counted off from an arbitrary value, Eq. (36) yields the following expression for reference points $\epsilon(0)_n^{\pm}$ of a quasi-particle energy and a antiquasi-particle energy

$$\epsilon(0)_n^{\pm} \equiv \pm a_n = \left(\text{Extr}\tilde{E}(k_1) \mp \Delta M_n(0)\right)/2. \tag{39}$$

Here one took into account that $N = 1$; an extremum of zone is redefined as $\text{Extr}\tilde{E}(k_1) = \text{Extr}E_n(k_1) - C_n$, the sign $\{\pm\}$ in left-hand side denotes a case of quasiparticles and antiquasi-particles, respectively; and the energy of particles in the pair is counted off from zero level.

One gets from the expression (39) that a_n is the energy which is required to create a pair from quasiparticle and antiquasiparticle when $k_1 = 0$ because

$$a_n = (\epsilon(0)_n^+ - \epsilon(0)_n^-)/2. \tag{40}$$

Because of an additional term $\tilde{\epsilon}_n(0)$ in a right-hand side of Eq. (35) we, generally speaking, cannot examine the left-hand side as a Hamiltonian operator of the quasi particles system acting on a corresponding wave function and as a consequence, can not construct a basis set of one-particle states of the problem. However, further we show, that $\hat{h}^{HF}$ is a Hamiltonian of an electron - hole pair.

Non-relativistic case

One can examine in non-relativistic limit quantum systems which are characterized by a small value of $\Delta M_n(0)$:

$$\Delta M_n(0) \to 0. \tag{41}$$

It means that weak many-particle effects occur and, accordingly, we can speak about a "light" electron. The equality (39) occurs under condition of (41)only in the case if $a_n = 0$. From here it follows, that the energy a_n of a pair is equal to zero. In other words, the energy is not expended to create an electron - hole pair.

Substituting Eqs. (38), (41) into Eq. (35) and taking into account the condition $a_n = 0$, one gets the Schrödinger equation as

$$\hat{h}^{HF}(r_1)\psi_n(r_1) = \tilde{\tilde{\epsilon}}_n\psi_n(r_1), \tag{42}$$

which describes the quasiparticle - antiquasiparticle pair (a non-relativistic electron - hole pair). Here $\tilde{\tilde{\epsilon}}_n = \tilde{\epsilon}_n - C$.

Since the energy a_n, expended on creation of a pair, equals to zero we have proved that the variable $\tilde{\tilde{\epsilon}}_n$ can be understood as the energy of an electron - hole pair. Therefore, Eq. (42) has a group of dynamic symmetry, which algebra is so(3) so(3) $\sim$ so (4) if to neglect an exchange interaction. As is known, a nonrelativistic hydrogen-like atom possesses such symmetry. Hence, we have proved that to calculate quasiparticle states in the non-relativistic case it is possible to use a basis set of states of a nonrelativistic hydrogen-like atom.

However, for a heavy electron $\Delta M_n(0) \geq 1$ according to the formula (40) we always have

$$a_n = -\Delta M_n(0)/2 \tag{43}$$

and, hence, there does not exist equation such as Schrödinger one for its describing. From here we conclude that the heavy electron can not be examined in a nonrelativistic limit.

Relativistic case

Let us generalize the proposed approach to relativistic case. To do it we substitute Eqs. (38) and (43) into (35) and let n tends to $n \to \infty$:

$$\hat{h}^{HF}(r_1)\psi_n(k_1r_1) = \left(\frac{\Delta M_n(0)}{2} + \tilde{\tilde{\epsilon}}_n(k_1)\right)\psi_n(k_1r_1), \quad n \to \infty. \tag{44}$$

Then, one can assume that the operator $\frac{\partial}{\partial t} - \hat{h}^{HF}$ in Eq. (44) is a quasirelativistic hamiltonian written in the implicit form in the Hartee - Fock approximation.

From consideration carried out above it follows that the desired relativistic equation of motion should describe a charged composite system from a pair of particles and have the

dynamic symmetry SO(4). A spin of given quantum system should be equal 1 as motion of a hole is a motion of an electron in many-particle positively charged matrix. In [10] the equation of motion of a relativistic charged vector boson has been found and shown, that it describes a relativistic hydrogen-like atom. The relativistic charged vector-boson appears a composite system with a corresponding spectrum of masses and in quasirelativistic limit $n \to \infty$ its energy E_1 is determined by the expression:

$$E_1 \approx \frac{m}{2} - \frac{m\gamma^2}{2n^2} - \frac{m\gamma^4}{8n^3}\left(\frac{4}{|k|} - \frac{3}{n}\right) - \frac{m\gamma^6}{8n^4}\left(\frac{3}{n^2} - \frac{8}{n|k|} + \frac{4}{k^2}\right) + O(\gamma^8).$$
(45)

Comparison of right-hand sides of formulas (44) and (45) yields that $\Delta M_\infty \equiv \lim_{n\to\infty} \Delta M_n(0) = m$ is a rest mass m of an electron. Hence, Eq. (44) is an equation of motion for a relativistic electron - hole pair with a reduced mass $\Delta M_\infty/2 = m/2$ which, apparently, is the relativistic charged vector-boson considered in quasirelativistic limit $n \to \infty$.

5 Conclusion

So, the variation method to find interacting quasiparticle states in crystals was developed. The quasiparticle propagator was constructed by summation over elements of secondary quantized density matrix. This approach allows us to find motion equations of one-electron states of excited atom in crystals.

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